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Single-Laboratory Evaluation of EPA (Environmental Protection Agency) Method 8080 for Determination of Chlorinated Pesticides and Polychlorinated Biphenyls in Hazardous Wastes (Journal Version)

Acurex Corp., Mountain View, CA

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16. ABSTRACT
Method 8080, as published in the Second Edition of "Test Methods for Evaluating Solid Waste," EPA Manual SW-846, has been evaluated in a single-laboratory study. The Florisil procedure recommended in Method 8080 for sample cleanup does not separate organochlorine pesticides (OCPs) from the polychlorinated biphenyls (PCBs). Consequently, gas chromatographic analysis of OCPs on the packed column recommended in the method may result in false identifications or in no identifications at all when PCBs are present. Therefore, silica gel was substituted for Florisil, a capillary column was substituted for the packed column, and a sulfur cleanup procedure was incorporated in the method. The revised method was evaluated with samples spiked at 3 concentrations. Precision and accuracy data indicate that the revised mehtod can be reliably applied to the determination of OCPs and PCBs in liquid and solid matrixes. Detection limits for liquid matrixes range from 0.02 to 0.09 ug/L for OCPs and from 0.5 to 0.9 ug/L for PCBs. Detection limits for solid matrixes range from 1 to 6 ug/kg for OCPs and from 60 to 70 ug/kg for PCBs.

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Single-Laboratory Evaluation of EPA Method 8080 for Determination of Chlorinated Pesticides and Polychlorinated Biphenyls in Hazardous Wastes

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Method 8080, as published in the Second Edition of "Test Methods for Evaluating Solid Waste," EPA Manual SW-846, has been evaluated in a single-laboratory study. The Florisil procedure recommended in Method 8080 for sample cleanup does not separate organochlorine pesticides (OCPs) from the polychlorinated biphenyls (PCBs). Consequently, gas chromatographic analysis of OCPs on the packed column recommended in the method may result in false identifications or in no identifications at all when PCBs are present. Therefore, silica gel was substituted for Florisil, a capillary column was substituted for the packed column, and a sulfur cleanup procedure was incorporated in the method. The revised method was evaluated with samples spiked at 3 concentrations. Precision and accuracy indicate that the revised method can be reliably applied to the determination of OCPs and PCBs in liquid and solid matrixes. Detection limits for liquid matrixes range from 0.02 to 0.09 μg/L for OCPs and from 0.5 to 0.9 μg/L for PCBs. Detection limits for solid matrixes range from 1 to 6 μg/kg for OCPs and from 60 to 70 μg/kg for PCBs.

Organochlorine pesticides (OCPs) can be classified in 3 major subgroups on the basis of their molecular structures: cyclopentadienes, cyclohexanes, and DDTs. Toxaphene is a mixture of chlorinated camphenes containing approximately 67–69% chlorine. Polychlorinated biphenyls (PCBs) are complex mixtures consisting of combinations of the 209 possible chlorinated biphenyls. Commercial mixtures of PCBs manufactured in the United States are known as Aroclors 1016, 1221, 1232, 1242, 1248, 1254, and 1260. The first 2 digits represent the biphenyl moiety, and the last 2 digits indicate the weight percent of chlorine in the mixture; Aroclor 1016 is an exception because it is a chlorinated biphenyl that contains 41.5% chlorine.

OCPs and PCBs have been determined in environmental samples by gas chromatography (GC) with electron-capture detection (1) and by mass spectrometry (2–5). The electron-capture detector is preferred over the mass spectrometer because it is 2–3 orders of magnitude more sensitive (6). Because PCBs are extracted along with OCPs and because they interfere with the determination of OCPs whenever electron-capture detectors are used, their presence in extracts together with the OCPs needs to be minimized. Therefore, several cleanup techniques based on Florisil (7–10), alumina (11–13), and silica gel chromatography (13–15) have been developed.

EPA Method 8080 (16) provides sample extract cleanup and GC conditions for the determination of the OCPs and the PCBs listed in Table 1 in a variety of environmental samples including groundwater, liquids, and solids. Following solvent extraction of liquid samples in a separatory funnel (Method 3510) or in a continuous liquid-liquid extractor (Method 3520) and of solid samples in a Soxhlet extractor (Method 3540) or with a sonicator (Method 3550), the extracts are cleaned up by Florisil chromatography. Compounds are eluted from the Florisil column with 6, 15, and 50% ethyl ether in hexane. All compounds listed in Table 1 except 6 OCPs elute in Fraction I (6% ether in hexane). Of those 6 pesticides, 4 (dieldrin, endosulfan I, endrin, and endrin aldehyde) elute in Fraction II (15% ether in hexane), and 2 (endosulfan II and endosulfan sulfate) elute in Fraction III (50% ether in hexane). Endrin aldehyde has also been reported in Fraction III.

There is no mention in Method 8080 of possible overlapping of compounds between fractions and of the reproducibility of the elution pattern. Moreover, the fact that OCPs are not separated from PCBs after the Florisil cleanup suggests that such a scheme may be of little use for samples containing OCPs as well as PCBs. Thus, a preliminary evaluation of Method 8080 was conducted to determine the recoveries of OCPs and PCBs in the absence of matrix interferences, to determine the extent of overlapping of compounds between fractions, and to determine the efficiency of the Florisil cleanup scheme with real samples.

In the improvement phase of this study, a fractionation procedure was developed to separate PCBs from the bulk of the OCP compounds and, at the same time, to remove interfering compounds coextracted from the samples. Several extract cleanup procedures based on silica, alumina, silica gel/Celite, and Florisil/charcoal chromatography were investigated. Furthermore, a capillary GC method was developed, and a method for sulfur removal was incorporated.

Table 1. Compounds listed in EPA Method 8080

Compound[a]	Storet No.	CAS No.
α-BHC	39337	319-84-6
β-BHC	39338	319-85-7
γ-BHC (Lindane)	39340	58-89-9
δ-BHC	34259	319-86-8
Heptachlor	39410	76-44-8
Aldrin	39330	309-00-2
Heptachlor epoxide	39420	1024-57-3
γ-Chlordane	39350	57-74-9
Endosulfan I	34361	959-98-8
4,4'-DDE	39320	72-55-9
Dieldrin	39380	60-57-1
Endrin	39390	72-20-8
Endosulfan II	34356	33212-65-9
4,4'-DDD	39310	72-54-8
Endrin aldehyde	34366	7421-93-4
Endosulfan sulfate	34351	1031-07-8
4,4'-DDT	39300	50-29-3
4,4'-Methoxychlor	NA[b]	72-43-5
Toxaphene	39400	8001-35-2
Aroclor 1016	34671	12674-11-2
Aroclor 1221	39488	1104-28-2
Aroclor 1232	39492	11141-16-5
Aroclor 1242	39496	53469-21-9
Aroclor 1248	39500	12672-29-6
Aroclor 1254	39504	11097-69-1
Aroclor 1260	39508	11096-82-5

[a] Kepone is included in Method 8080 in the second edition of SW-846 but not in the third edition.
[b] Not available.

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Table 2. Distribution and percent recoveries of OCPs and PCBs in silica gel column fractions[a] (average of 3 determinations ± SD)[b]

Compound	Fraction I		Fraction II		Fraction III		Total recovery	
	Concn 1	Concn 2	Concn 1	Concn 2	Concn 1	Concn 2	Concn 1	Concn 2
α-BHC					82 (1.7)	74 (8.0)	82 (1.7)	74 (8.0)
β-BHC					107 (2.1)	98 (12.5)	107 (2.1)	98 (12.5)
γ-BHC					91 (3.6)	85 (10.7)	91 (3.6)	85 (10.7)
δ-BHC					92 (3.5)	83 (10.6)	92 (3.5)	83 (10.6)
Heptachlor	109 (4.1)	118 (8.7)					109 (4.1)	118 (8.7)
Aldrin	97 (5.6)	104 (1.6)					97 (5.6)	104 (1.6)
Heptachlor epoxide					95 (4.7)	88 (10.2)	95 (4.7)	88 (10.2)
Endosulfan I					95 (5.1)	87 (10.2)	95 (5.1)	87 (10.2)
4,4'-DDE	86 (5.4)	94 (2.8)					86 (5.4)	94 (2.8)
Dieldrin					96 (6.0)	87 (10.6)	96 (6.0)	87 (10.6)
Endrin					85 (10.5)	71 (12.3)	85 (10.5)	71 (12.3)
Endosulfan II					97 (4.4)	86 (10.4)	97 (4.4)	86 (10.4)
4,4'-DDD					102 (4.6)	92 (10.2)	102 (4.6)	92 (10.2)
Endrin aldehyde					81 (1.9)	76 (9.5)	81 (1.9)	76 (9.5)
Endosulfan sulfate					93 (4.9)	82 (9.2)	93 (4.9)	82 (9.2)
4,4'-DDT			86 (13.4)	73 (9.1)	15 (18.7)	8.7 (15.0)	101 (5.3)	82 (23.7)
4,4'-Methoxychlor					99 (9.9)	82 (10.7)	99 (9.9)	82 (10.7)
Aroclor 1016	86 (4.0)	87 (6.1)					86 (4.0)	87 (6.1)
Aroclor 1260	91 (4.1)	95 (5.0)					91 (4.1)	95 (5.0)
Tech. chlordane	14 (5.5)	22 (5.3)	19 (6.8)	39 (3.6)	29 (5.0)	37 (5.1)	62 (3.3)	98 (1.9)
Toxaphene			15 (2.4)	17 (1.4)	73 (9.4)	84 (10.7)	88 (12.0)	101 (10.1)

[a] Eluant composition: Fraction I, 80 mL hexane; Fraction II, 50 mL hexane; Fraction III, 15 mL methylene chloride; concentration 1 is 0.5 μg per column for BHCs, heptachlor, aldrin, heptachlor epoxide, endosulfan I; 1.0 μg per column for dieldrin, endosulfan II, 4,4'-DDT, endrin aldehyde, 4,4'-DDD, 4,4'-DDE, endrin, and endosulfan sulfate; 5 μg per column for 4,4'-methoxychlor and technical chlordane; 10 μg per column for toxaphene, Aroclor 1016, and Aroclor 1260. For concentration 2, amounts spiked are 10 times higher than for concentration 1.

[b] Recovery cutoff point is 5%. Data obtained with standards dissolved in 2 mL hexane.

With the use of silica gel fractionation and the added resolution achieved with a capillary column, all OCPs listed in Table 1, except toxaphene, were determined. Evaluation studies included only Aroclors 1016 and 1260.

Experimental

Apparatus and Materials

(a) *Glassware.*—Separatory funnel, 500 mL, with Teflon stopcock; glass drying column, 21 cm × 4.5 cm id, plugged with glass wool; Kuderna-Danish evaporative flask, 500 mL, with 10 mL graduated concentrator tube and 3-ball macro Snyder column; wide-mouth amber glass bottle, 500 mL, with Teflon-lined screw cap; glass cleanup column, 20 cm × 11 mm id, with 200 mL reservoir and Teflon stopcock.

(b) *Water bath.*—With concentric ring cover; heat to 98 ± 2°C.

(c) *Sonicator.*—Model W-375 (Heat Systems Ultrasonics, Inc.).

(d) *Gas chromatograph.*—Equipped with constant-current pulsed-frequency electron-capture detector and data system. Operating conditions: injection port 225°C; detector 350°C; flow rates for carrier (helium at 16 psi for DB-5 column and nitrogen at 20 psi for SPB-608 column) and detector make-up gas (nitrogen) at 30 mL/min; splitless mode with splitless valve on for 30 s.

(e) *GC columns.*—(*1*) DB-5 fused-silica capillary column, 30 m × 0.25 mm id (J&W Scientific Inc., Folsom, CA), film thickness 0.25 μm. Temperature program: initial 100°C, hold 2 min, programming rate 1, 15°C/min (100°C to 160°C); programming rate 2, 5°C/min (160°C to 270°C). (*2*) SPB-608 fused-silica capillary column, 30 m × 0.25 mm id (Supelco Inc., Bellefonte, PA), film thickness 0.25 μm. Temperature program: initial 160°C, hold 2 min, programming rate 5°C/min (160°C to 290°C), hold 1 min at 290°C.

(f) *Autosampler.*—Varian Model 8000, 2 μL injection volume.

(g) *Glass wool.*—Pyrex Fiberglas sliver, 8 μm. Soxhlet-extract overnight with methylene chloride.

Reagents

(a) *Solvents.*—Methylene chloride, hexane, acetone, toluene, 2-propanol; all pesticide grade, distilled in glass.

(b) *Sodium sulfate.*—ACS grade, granular, anhydrous. Purify by heating 4 h at 400°C in shallow tray.

(c) *Deactivated silica gel.*—3.3%. Activate silica gel PR grade (Davidson 923, 100–200 mesh, Supelco Inc., Bellefonte, PA) 16 h at 130°C. Deactivate adsorbent by adding 3.3 mL water to 96.7 g activated silica gel. Equilibrate 6 h after addition of water. Store in tightly capped glass container; do not keep for more than 1 week. Suitability test: Using procedure outlined in *Silica Gel Cleanup*, load test column with 2 mL standard in hexane and collect 3 fractions: elute Fraction I with 80 mL hexane, Fraction II with additional 50 mL hexane, and Fraction III with 15 mL methylene chloride. Concentrate fractions and determine percent recovery. Recoveries should be ≥70%, and elution patterns should match those given in Table 2. Report results of test column with all samples that were cleaned up with a given batch of silica gel.

(d) *Tetrabutyl ammonium sulfite reagent.*—Extract solution of 3.39 g (0.01 mol) tetrabutyl ammonium hydrogen sulfate in 100 mL water with three 20 mL portions of hexane (to remove impurities), and then add 25 g anhydrous sodium sulfite (analytical grade).

(e) *Pesticide and PCB standards.*—Obtain from U.S. EPA Quality Assurance Materials Bank, Research Triangle Park, NC, or from manufacturers; use without further purification (purity > 98%). Prepare stock solutions at 2000 ng/μL in toluene–hexane (1 + 1) for all compounds listed in Table 1 except methoxychlor and PCBs. Prepare methoxychlor standard in methylene chloride at 5000 ng/μL and PCB standards in hexane at 2500 ng/μL. Prepare mixture of all OCPs in

hexane at 0.05 ng/μL, 0.1 ng/μL, and 0.5 ng/μL for GC calibration. Store solutions at 4°C in the dark.

Sample Collection

Liquid waste was collected from a pesticide waste storage facility at a California agricultural field station. This waste contains high concentrations of organics (total organic carbon, 520 mg/L; total organic halogen, 30 mg/L).

The standard reference material is identified as NBS SRM-1645. According to the National Bureau of Standards, the material was dredged from the bottom of the Indiana Harbor Canal near Gary, IN. The material was screened to remove foreign objects, freeze-dried, sieved (particle size < 180 μm), and sterilized by radiation to minimize biological activity. Physicochemical characterization of the NBS SRM-1645 is given by Lopez-Avila et al. (17).

Sandy loam was obtained from Soils Inc., Puyallup, WA, and had the following physicochemical characteristics: pH 5.9–6.0; 89% sand, 7% silt, 4% clay; cation exchange capacity, 7.5 meq/100 g; total organic carbon content, 1290 ± 185 mg/kg.

Sample Extract Preparation

Extract 300 mL liquid sample at neutral pH in separatory funnel with 60 mL methylene chloride. Repeat extraction twice. Combine extracts, dry by passing through column of anhydrous sodium sulfate, and concentrate in Kuderna-Danish evaporator to less than 10 mL. Add 50 mL hexane to concentrate, and reevaporate until volume is reduced to 30 mL.

Weigh 30 g soil or sediment and place in wide-mouth bottle. Extract sample with 60 mL hexane–acetone (1 + 1) by sonicating 3 min. Repeat extraction twice, each time for 3 min and with fresh portions of hexane–acetone (1 + 1). Combine extracts, dry by passing through column of anhydrous sodium sulfate, and concentrate in Kuderna-Danish evaporator to less than 10 mL. Add 50 mL hexane to concentrated extract and reevaporate until volume is reduced to 30 mL.

Use 30-mL concentrates as follows: 2 mL for background analysis; spike three 6 mL portions with 1500 ng, 3000 ng, and 15 000 ng, respectively, with OCPs listed in Table 1 and with 15 000 ng, 30 000 ng, and 150 000 ng each of Aroclor 1016 and 1260. Keep 10 mL as backup material. Do not spike all 7 PCB mixtures listed in Table 1, because method does not allow quantitation of all PCBs in the presence of OCPs. Spike only Aroclor 1016 and Aroclor 1260 together with OCPs.

Split each spiked 6 mL extract portion into three 2 mL aliquots for triplicate GC analysis.

Silica Gel Cleanup

Fill 20 cm × 11 mm id glass cleanup column with 3 g 3.3% deactivated silica gel. Top column with 2–3 cm anhydrous sodium sulfate. Rinse column with 10 mL hexane, and discard eluate. Quantitatively transfer sample extract (2 mL) to prepared column and follow with several hexane rinses of 1–2 mL each. Elute column with 80 mL hexane at a rate of ca 5 mL/min. Remove collection flask and label as Fraction I. Elute column with additional 50 mL hexane, collect eluate, and label as Fraction II. Perform third elution with 15 mL methylene chloride (Fraction III). Concentrate 3 fractions in Kuderna-Danish evaporators. Exchange methylene chloride (Fraction III) for hexane. Adjust final volume of each fraction to 10 mL.

Elemental Sulfur Removal

Shake hexane extract (2 mL) with 1 mL 2-propanol and 1 mL tetrabutyl ammonium sulfite reagent for at least 1 min. Add ca 100 mg sodium sulfite crystals. If sodium sulfite disappears, add more sodium sulfite in 100 mg portions until solid residue remains after repeated shaking. Add 5 mL water and shake test tube for another 1 min. Centrifuge mixture and transfer hexane layer to another vial for analysis.

Gas Chromatography

Inject 1 μL aliquots into GC apparatus set up with DB-5 fused-silica capillary column (*1*). Program oven as described under apparatus (e). Perform 3-level calibration using multicomponent standards containing OCPs at 0.0125 to 0.025 ng/μL (for low-level standard) and Aroclor 1016/1260 at 0.5 ng/μL (for low-level standard). Medium-level standard and high-level standards should contain OCPs or PCBs at 2 and 5 times the concentration of low-level standards, respectively. Run toxaphene standards separately at 0.1 ng/μL, 0.5 ng/μL, and 1.0 ng/μL. Alternate sample injections with OCP standards at 0.05 to 0.1 ng/μL and Aroclor 1016/1260 standards at 0.5 ng/μL. Dilute samples with hexane to bring detector response within calibration curve. Quantitate OCPs by using peak areas rather than peak heights. For multicomponent mixtures such as PCBs and toxaphene, match retention times of peaks in standards with peaks in samples. Quantitate 6–8 major peaks, add peak areas, and calculate as total response in sample vs total response in standard. Peaks that were used in quantitation of PCBs are identified in Table 3. For toxaphene, use peaks at retention times 20.564, 22.332, 23.675, 24.681, 26.246, and 27.322 min.

Method Precision, Accuracy, and Detection Limit

Process fortified extracts of environmental samples through silica gel fractionation scheme given above. Perform each experiment in triplicate at a minimum of 3 concentrations. Determine method detection limit by the procedure of Glazer et al. (18).

Results and Discussion

Florisil Fractionation

Florisil fractionation was performed as recommended in Method 8080 (16). Separate experiments were run in duplicate for PCBs, toxaphene, technical chlordane, OCP group A (γ-BHC, heptachlor, aldrin, heptachlor epoxide, endosulfan I, dieldrin, endosulfan II, 4,4′-DDT, and endrin aldehyde), and OCP group B (α-BHC, β-BHC, δ-BHC, 4,4′-DDE, endrin, 4,4′-DDD, endosulfan sulfate, and 4,4′-methoxychlor). Experimental results are presented in Table 4.

Overall recoveries are quantitative, and agreement between duplicate experiments is, in most cases, excellent. However, the following discrepancies were found between our data and the recovery data given in Method 8080: (a) dieldrin did not elute 100% in Fraction II but was recovered in Fraction I as well as II, (b) more endosulfan I was recovered in Fraction I than in Fraction II, (c) more endosulfan II was recovered in Fraction II than in Fraction III, (d) endrin overlapped in Fractions I and II, and (e) endosulfan sulfate overlapped in Fractions II and III.

A possible explanation for these discrepancies might be the fact that the Florisil calcination temperature is critical for the Florisil adsorption properties (8). Difficulties in obtaining reproducible recoveries and the overlapping of pesticides between fractions have also been reported by others (8–10).

Table 3. Summary of retention times (min) for PCBs[a]

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Pesticide eluting at same retention time
1		8.396						
2		9.149	9.146					
3		10.308	10.306					
4	10.949	10.959	10.957	10.963				
5	11.722	11.732	11.730	11.734				
6	12.060[b]	12.068	12.066	12.071				
7	12.256	12.262	12.262	12.267	12.254			
8	12.933		12.939	12.944				
9		13.573	13.574					
10	13.683[b]	13.685	13.687	13.691	12.679			
11	13.756	13.763	13.761	13.756	13.753			
12	14.048		14.053	14.057				
13	14.341[b]	14.344	14.346	14.351	14.337			
14	14.960		14.963	14.971	14.954			
15	15.055		15.061	15.066				
16	15.260[b]	14.258	15.262	15.267	15.252			
17	15.310	15.309	15.314	15.319	15.305			
18	15.652[b]	15.648	15.653	15.661	15.645			
19	15.860			15.865	15.852			
20	15.924	15.923	15.928	15.93	15.919		15.928	heptachlor (15.91 ± 0.008)
21	16.116		16.118	15.123	16.111			
22	16.398		16.400	16.406	16.390			
23	16.540[b]		16.542	16.551	16.534	16.548	16.542	
24		16.574						
25		16.604						
26	16.702	16.699	16.701	16.713	16.699	16.710	16.706	
27	16.818		16.821	16.828	16.808	16.814		
28	16.843		16.847	15.841				
29			17.142				17.141	
30	17.290		17.298	17.303	17.289	17.302	17.299	
31	17.427	17.414	17.427	17.431	17.418	17.426	17.403	
32	17.704		17.703	17.711				
33	17.755[b]		17.755	17.759	17.745	17.758	17.573	
34	18.048		18.048	18.055	18.040			
35	18.253		18.254	18.263				
36							18.356	
37				18.459	18.468	18.456		
38							18.555	
39	18.606		18.602	18.611	18.598	18.610		heptachlor epoxide (18.60 ± 0.009)
40	18.736		18.732	18.743	18.728	18.738	18.738	
41	18.881		18.875	18.886	18.868			
42			18.898				18.908	
43	19.147			19.150	19.136	19.147		
44				19.203				
45	19.503		19.500	19.514	19.498			γ-chlordane (19.48 ± 0.012)
46							19.542	
47			19.690	19.697	19.682			
48			19.749	19.760	19.742		19.757	
49	19.939		19.951	19.960	19.943	19.954	19.952	endosulfan (19.94 ± 0.010)
50				20.179		20.188	20.172	
51					20.357	20.362	20.363	
52			20.551	20.567	20.553	20.556	20.560	
53			20.745	20.755	20.738	20.744	20.757	
54	20.909		20.909	20.919	20.902	20.911	20.917	dieldrin (20.91 ± 0.008)
55							21.023	
56			21.112	21.127	21.106	21.116	21.122	
57			21.537	21.552	21.529	21.550		
58							21.587[b]	
59					21.751	21.750	21.752[b]	
60					21.894	21.897	21.887	
61		22.017			22.012			
62						22.025	22.030	
63	22.047							endosulfan II (22.05 ± 0.006)
64			22.083	22.097	22.077	22.086		
65						22.428	22.428[b]	
66					22.501	22.508		
67						22.585	22.589	
68						22.704	22.712	
69	22.752							endrin aldehyde (22.75 ± 0.007)
70		22.927		22.936	22.922	22.930	22.935	
71		23.039					23.043	
72			23.073	23.085	23.071	23.069		
73					23.395	23.401	23.407	
74							23.486	
75	23.664	23.654				23.664	23.665	

Table 3. Continued

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Pesticide eluting at same retention time
76						23.758	23.758	
77		23.955		23.969	23.950	23.959	23.962	
78						24.060	24.066[b]	
79						24.265	24.289	
80						24.509	24.504	
81				24.606	24.586	24.591	24.600	
82						24.783	24.786	
83						24.986	24.996	
84							25.185	
85						25.459	25.463[b]	
86						25.666	25.670	
87						25.857	25.841	
88						26.070	26.088	
89						26.241	26.247[b]	
90							26.368	
91				26.487	26.478	26.480	26.486	
92							26.583	
93							26.739	
94							26.954	
95							27.283	
96					27.564	27.567	27.575[b]	
97							27.777	
98							27.898[b]	
99							28.095	
100							28.639	
101							28.789	
102							29.264	
103							29.545	
104							29.643	
105					30.077		30.084[b]	
106							30.334	

[a] Single determinations on DB-5 column. GC operating conditions are given in the Experimental section.
[b] Peak used in quantitation.

Regardless of the reproducibility of the fractionation, it is apparent that the Florisil fractionation method is not suitable for samples that contain OCPs and PCBs. PCBs appear in the same fraction as the bulk of the OCP compounds, but these 2 types of compounds need to be separated from each other to a larger extent to avoid cross-interference. To exemplify this on a real sample, we extracted a liquid waste and spiked the extract with known amounts of OCPs and Aroclors 1016 and 1260. Figures 1 and 2 show GC/EC chromatograms of each of the 3 fractions (unspiked and spiked extract). Because of the complexity of this sample matrix, fractions were analyzed on a DB-5 capillary column; however, even then spiking compounds could not be determined. In view of these results, we eliminated the Florisil fractionation scheme from further evaluation.

Silica Gel Fractionation

Silica gel fractionations were performed in triplicate at 2 concentration levels according to a procedure developed by Biddleman et al. (15), with slight modifications, as detailed in the experimental section. Technical chlordane and toxaphene fractionations were performed separately. Distribution and percent recoveries of the OCPs, Aroclor 1016, Aroclor 1260, technical chlordane, and toxaphene, are given in Table 2. Distribution patterns of OCPs and PCBs in the 3 silica gel fractions were quite reproducible. Compounds found to elute in Fraction I (80 mL hexane) include heptachlor, aldrin, 4,4′-DDE, and the PCBs. Almost all other OCPs elute in Fraction III.

Total recoveries were >70%, except for technical chlordane at concentration 1, with most values ranging from 80 to 110% (Table 2). The GC/EC chromatograms of the silica gel Fractions I, II, and III for the unspiked and spiked liquid waste extract are shown in Figures 3 and 4.

Evaluation of silica gel fractionation scheme with real sample extracts (e.g., liquid waste, NBS SRM-1645, sandy loam) gave comparable results (19). Only a few compounds (4,4′-

Table 4. Recoveries (%)[a] of organochlorine pesticides and PCBs from spiked samples following Florisil fractionation

	Spike level, μg	Fraction I	Fraction II	Fraction III	Total
α-BHC	0.5	94; 92	9.7; 8.7		104; 101
β-BHC	0.5	86; 83	10; 0		96; 83
γ-BHC	0.5	76; 77	8.5; 8.1	1.5; <1.0	86; 85
δ-BHC	0.5	70; 60	31; 27		101; 87
Heptachlor	0.5	75; 78	5.3; 5.8		80; 84
Aldrin	0.5	78; 80	6.0; 6.6	2.8; 3.8	87; 90
Heptachlor epoxide	0.5	79; 80	15; 15		94; 95
Endosulfan I	0.5	59; 64	29; 30		88; 94
4,4′-DDT	1.0	95; 95	8.7; 6.7		104; 102
Dieldrin	1.0	20; 24	71; 70		91; 94
Endrin	1.0	37; 43	64; 51		101; 94
Endosulfan II	1.0		60; 79	30; 15	90; 94
4,4′-DDD	1.0	93; 90	11; 10		104; 100
Endrin aldehyde	1.0		80; 90	11; 4.4	91; 94
Endosulfan sulfate	1.0		23; 23	57; 51	80; 74
4,4′-DDE	1.0	97; 93	9.6; 8.6		107; 102
4,4′-Methoxychlor	5.0	87; 84	29; 26		116; 110
Aroclor 1016	10.0	86; 76	4.6; 4.4		91; 80
Aroclor 1260	10.0	91; 78	10; 9.0		101; 87
Tech. chlordane	5.0	93; 94	9.6; 7.6		103; 102
Toxaphene	10.0	105; 108			105; 108

[a] $N = 2$.

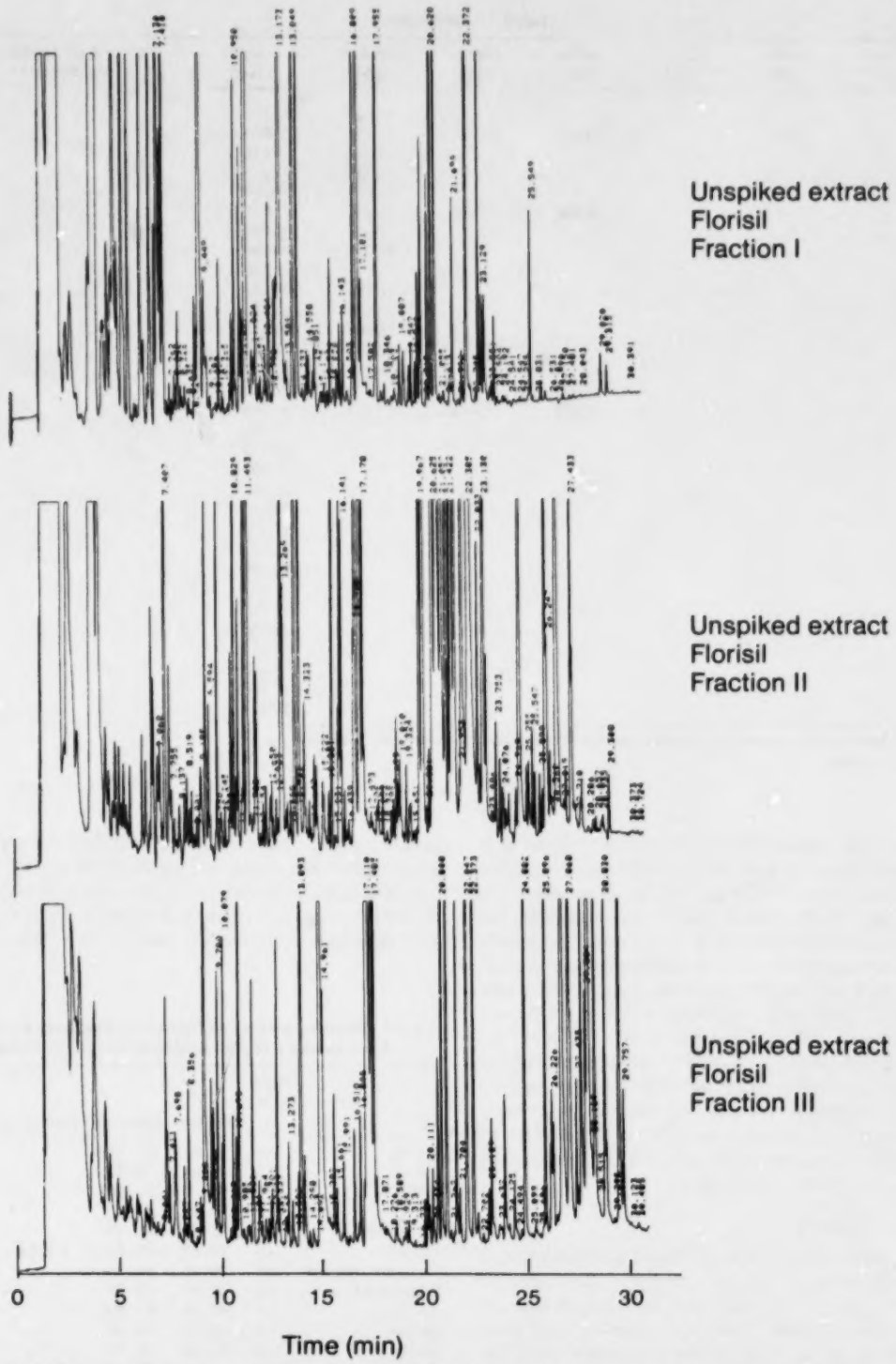

Figure 1. GC/EC chromatograms of Florisil Fractions I (top), II (middle), and III (bottom) of liquid waste extract analyzed on 30 m × 0.25 mm id DB-5 fused-silica capillary column.

DDD, α-BHC, γ-chlordane) were split between fractions when the real samples were fractionated.

These results show that Fractions II and III may be combined before concentration and analysis, when the sample matrixes are relatively simple. However, when samples with complex matrixes have to be extracted, especially matrixes containing organic solvents, more crossover between fractions may occur. In such cases, it is more advantageous to analyze the 3 fractions separately.

Sulfur Removal

Elemental sulfur, which may be present in extracts from sediments and from some industrial samples, gives GC peaks that mask the region of aldrin, BHCs, heptachlor, and hep-

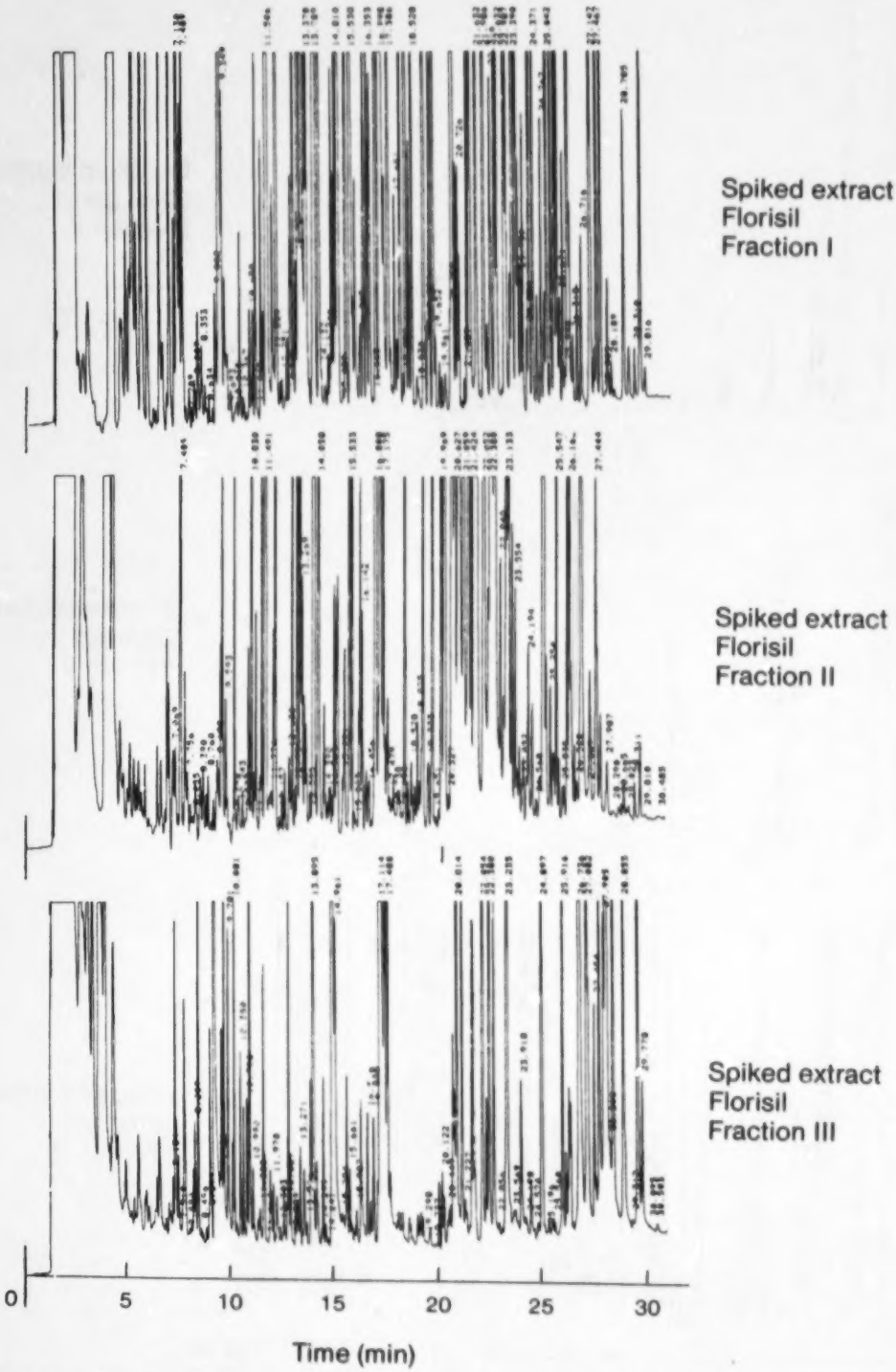

Figure 2. GC/EC chromatograms of Florisil Fractions I (top), II (middle), and III (bottom) of liquid waste extract spiked with OCPs and PCBs and analyzed on the 30 m × 0.25 mm id DB-5 fused-silica capillary column.

tachlor epoxide when the analysis is performed on the 1.5% OV-17/1.95% OV-210 on Chromosorb-WHP or on the 30 m DB-5 fused-silica capillary column.

Several methods are available for the removal of sulfur from extracts (20–24). Shaking with 0.1–0.2 mL metallic mercury (20) is simple, but it does not remove all the sulfur. Although Goerlitz and Law (20) claimed that aldrin, dieldrin, heptachlor, lindane, and 4,4'-DDT were not affected by mercury, Thompson (21) reported that recovery of heptachlor was only 40% when mercury was used for sulfur removal. Activated copper (22) and Raney nickel (23) have also been used to remove sulfur. Jensen and co-workers (24) used tetra-

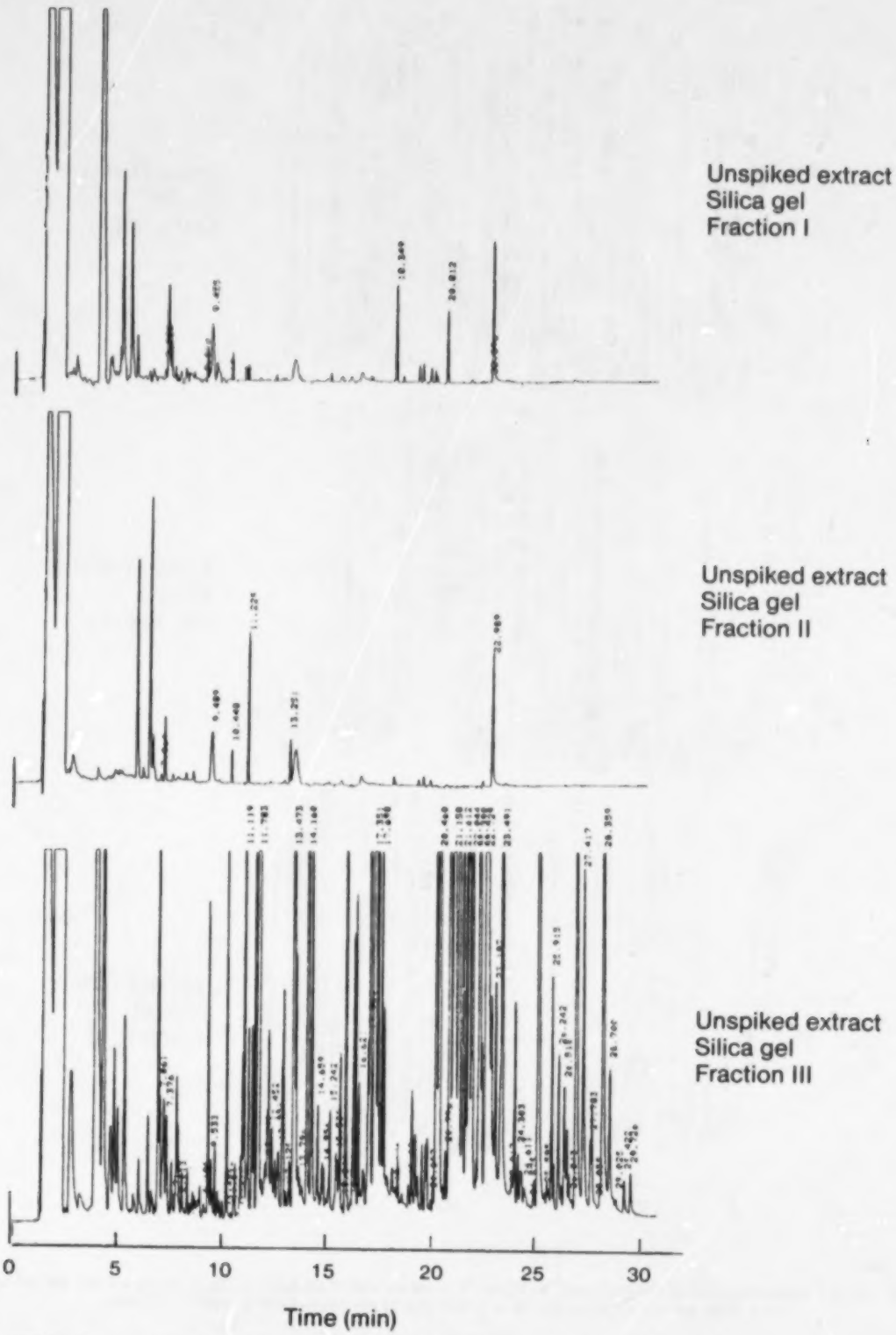

Figure 3. GC/EC chromatograms of silica gel Fractions I (top), II (middle), and III (bottom) of liquid waste extract analyzed on 30 m × 0.25 mm id DB-5 fused-silica capillary column.

butyl ammonium sulfite and reported recoveries >90% for DDT, DDD, DDE, and PCBs, and recoveries of 73–79% for aldrin and γ-BHC.

We have used the Jensen et al. procedure (24) on 5 real sample extracts fortified with OCPs and PCBs to determine if removal of sulfur is affected by matrix interferences and if OCP and PCB recoveries are acceptable (>80%). In addition to the real sample extracts, 3 pesticide standards were treated

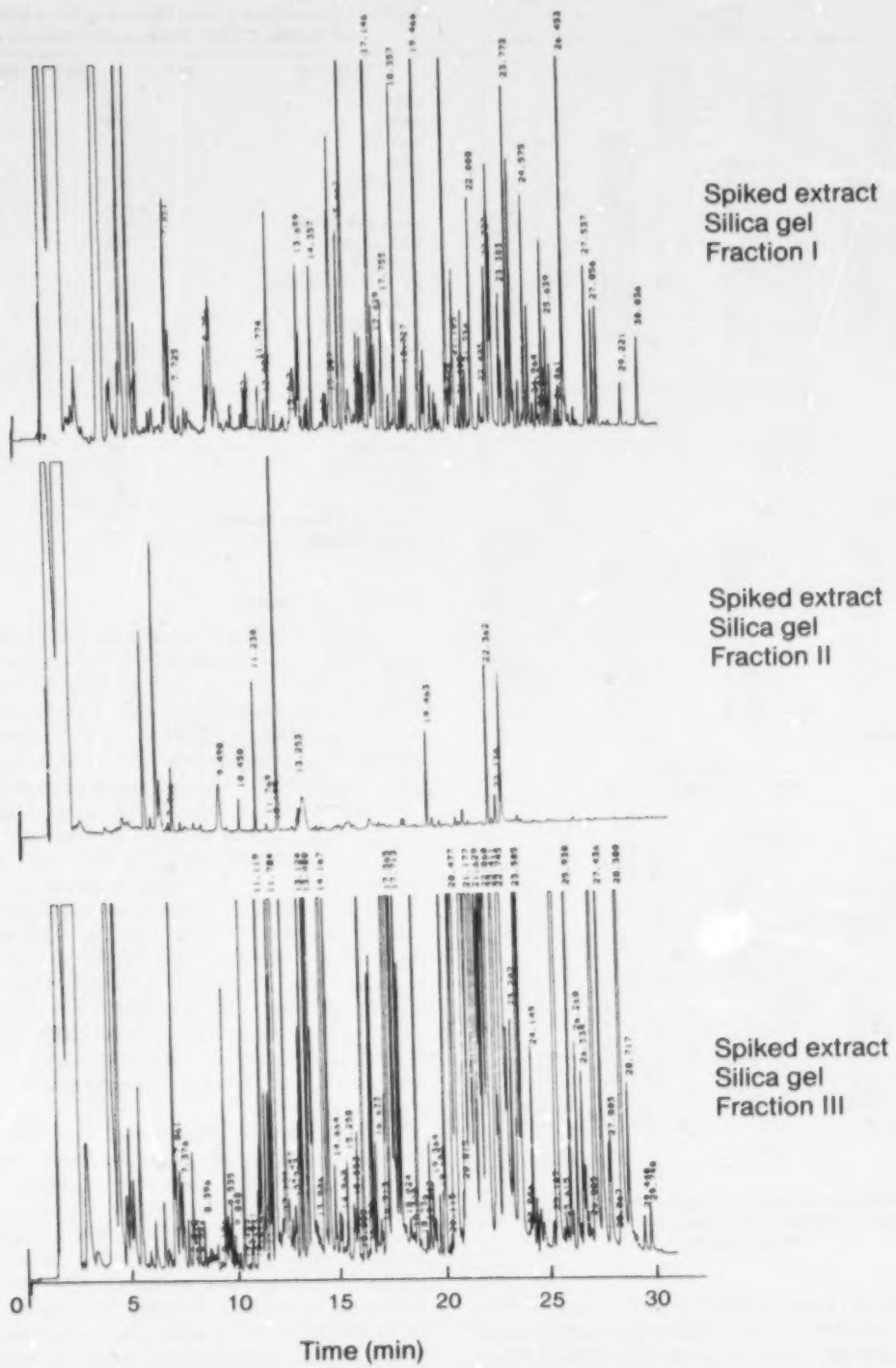

Figure 4. GC/EC chromatograms of silica gel Fractions I (top), II (middle), and III (bottom) of liquid waste spiked with OCPs and PCBs and analyzed on 30 m × 0.25 mm id DB-5 fused-silica capillary column.

with the tetrabutyl ammonium sulfite reagent to determine compound recovery in the absence of matrix interferences.

Results are presented in Table 5. Examination of the gas chromatograms showed that sulfur was removed quantitatively regardless of the matrix; therefore, this procedure is recommended for incorporation into the revised method protocol. Endrin aldehyde recovery was only about 10%, possibly because of the presence of sulfite.

Capillary GC

The GC retention times of 18 OCPs on the DB-5 and the SPB-608 fused-silica capillary columns are presented in Ta-

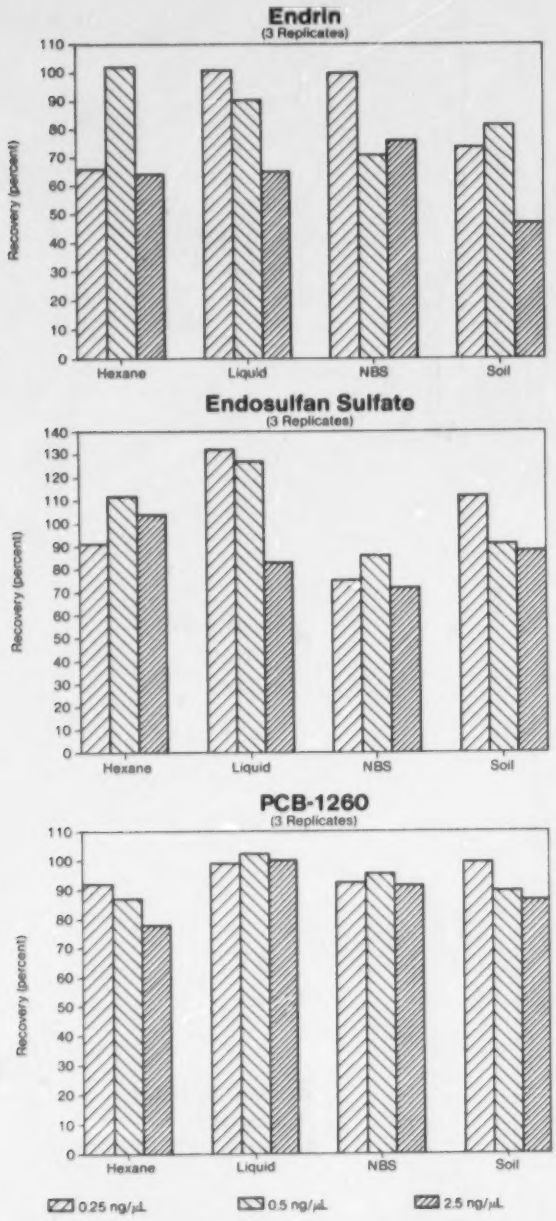

Figure 5. Distribution of average recoveries for endrin (top), endosulfan sulfate (middle), and Aroclor 1260 (bottom) for revised Method 8080.

ble 6. Toxaphene is not included because of its multipeak response. Aroclor mixtures have been analyzed individually on the DB-5 column; retention times of individual chlorinated biphenyls in these mixtures are given in Table 3.

We have indicated in Table 3 which of the OCPs elute at the same retention times as some of the components of the Aroclor mixtures. Of the 6 OCP peaks that overlap with PCB component peaks, only heptachlor and γ-chlordane are of concern, because the other 4 compounds are separated from PCBs during the silica gel chromatography step. The heptachlor peak overlaps with a PCB peak eluting at 15.91 ± 0.008 min (present in 6 of the 7 PCB mixtures), and the γ-chlordane peak overlaps with a PCB peak eluting at 19.48 ± 0.012 min (present in 4 of the 7 PCB mixtures).

Table 5. Recoveries (%) of OCPs and PCBs following reaction of standards[a] with tetrabutyl ammonium sulfite

Compound	Without sulfur added[a]	With sulfur added[b]
α-BHC	110	103
β-BHC	106	99
γ-BHC	112	108
δ-BHC	100	86
Heptachlor	103	97
Aldrin	104	99
Heptachlor epoxide	107	101
γ-Chlordane	98	100
Endosulfan I	108	106
4,4′-DDE and Dieldrin	91	103
Endrin	87	89
Endosulfan II	99	99
4,4′-DDD	103	106
Endrin aldehyde	10	8
Endosulfan sulfate	94	93
4,4′-DDT	86	90
4,4′-Methoxychlor	85	68
Toxaphene	93	83
Aroclor 1016	108	88
Aroclor 1260	87	68

[a] Average of 2 determinations.
[b] Single determination.

Method Performance

Method performance, as used here, includes the method precision, accuracy, and detection limit. To determine method precision and accuracy, clean hexane and extracts of environmental samples (a liquid waste, an NBS sediment SRM-1645, and a sandy loam soil sample) were spiked with OCPs listed in Table 1 (except toxaphene), with Aroclor 1016, and with Aroclor 1260 at 3 concentrations (0.25, 0.5, and 2.5 ng/μL for the OCPs and 2.5, 5.0, and 25 ng/μL for PCBs) and were processed through the method. Because of interference, δ-BHC, endosulfan II, and 4,4′-DDD could not be determined in the liquid waste when spiked at concentrations 1 and 2, endrin aldehyde could not be determined in the liquid waste at any of the 3 spike levels, and 4,4′-methoxychlor could not be determined in the NBS SRM-1645 when spiked at concentration 1. Spiked extracts rather than actual spiked samples were used in the determination of method precision and accuracy, because Method 8080 addresses only the GC analysis, including the extract cleanup step. Sample extracts were prepared according to procedures given in the 3500 series methods (16).

To summarize the significance of the results presented in Table 7, the interquartile ranges (defined by the data ranked within 25 to 75% of the total number of data points) of the average percent recoveries (method accuracy) and the relative standard deviations (RSD) (method precision) have been calculated. The interquartile range for method accuracy is 83–99% and for method precision is 5.4–14%.

No patterns between recovery and concentration of the OCPs and PCBs or the matrix were observed. Percent recovery of each compound as a function of matrix, for each of the 3 concentrations was plotted, but no trends were found. Figure 5 shows in a bar graph format how the recoveries of endrin, endosulfan sulfate, and Aroclor 1260 vary with compound concentration for each of the 4 matrixes. Likewise, RSDs of recoveries were plotted as a function of concentration for each of the 4 matrixes (Figure 6).

The method detection limits (MDL) are presented in Table 8. They were determined by subjecting 7 distilled water and 7 sandy loam soil samples containing the test compounds to the entire analytical process. Blank measurements for the distilled water and sandy loam soil were performed in trip-

Table 6. Summary of retention times (min) for organochlorine pesticides on fused-silica capillary columns[a]

Compound No.	Name	DB-5[b]	SPB-608[c]
1	α-BHC	12.29 ± 0.010	9.46
2	β-BHC	13.13 ± 0.009	11.33
3	γ-BHC	13.37 ± 0.011	10.97
4	δ-BHC	14.14 ± 0.011	12.73
5	Heptachlor	15.91 ± 0.008	12.46
6	Aldrin	17.16 ± 0.009	13.76
7	Heptachlor epoxide	18.60 ± 0.009	15.98
8	γ-Chlordane	19.48 ± 0.012	16.70
9	Endosulfan I	19.94 ± 0.010	17.40
10	4,4'-DDE	20.83 ± 0.008	18.36
11	Dieldrin	20.91 ± 0.008	18.60
12	Endrin	21.71 ± 0.007	19.96
13	Endosulfan II	22.05 ± 0.006	20.69
14	4,4'-DDD	22.38 ± 0.008	20.53
15	Endrin aldehyde	22.75 ± 0.007	21.90
16	Endosulfan sulfate	23.64 ± 0.008	22.54
17	4,4'-DDT	23.79 ± 0.008	21.72
18	4,4'-Methoxychlor	25.94 ± 0.007	24.90

[a] GC operating conditions are given in the Experimental section. Toxaphene and PCBs are not included because of their multipeak response.
[b] Values for DB-5 column are average retention time ± SD of 10 replicate determinations.
[c] Single determination.

licate. MDLs were computed from the SD of the 7 replicates and the Student's t value for a one-tailed test at the 99% confidence level (6 degrees of freedom). For water samples, MDLs ranged from 0.02 to 0.09 μg/L for OCPs and from 0.5 to 0.9 μg/L for PCBs. When using a 2 μL aliquot of a 10 mL extract (after silica gel fractionation) obtained from 1 L of water containing the test compounds, the amounts injected onto the GC column ranged from 4 to 18 pg for OCPs and from 100 to 180 pg for PCBs. For soil samples, MDLs ranged from 1 to 6 μg/kg for OCPs and from 60 to 70 μg/kg for PCBs. When using a 2 μL aliquot of a 10 mL extract (after silica gel fractionation) obtained from 10 g soil sample containing the test compounds, the amounts injected onto the GC column ranged from 2 to 12 pg for OCPs and from 120 to 140 pg for PCBs. These amounts are sufficient for identifying the compounds, since our low-level calibration standard contains 12.5 to 25 pg/μL for OCPs and 500 pg/μL for PCBs, and we usually inject 2 μL.

Detection limits lower than those given in Table 8 may be achievable with larger samples (typical sample volume for aqueous samples is 1 L; typical wet sample weight for solids is 10 g) and by concentrating the extracts to 0.5 mL instead of 10 mL. Except for heptachlor epoxide and endosulfan sulfate, our detection limits are higher than those reported for EPA Method 608 (1) because the final volume of the silica gel fractions was 10 mL. However, no interfering peaks coeluted with any of the test compounds to require background correction, and Aroclors 1016 and 1260 were measured in the presence of OCPs. Recoveries in the range of 58–134% were achieved for water samples, and they were similar to those measured at higher concentrations. In the case of the sandy loam soil sample, OCPs recoveries were lower (15–47%), probably because of sorption onto soil.

The revised Method 8080 presented here has been evaluated in a single laboratory with a few relevant liquid and solid wastes. However, the revised method should be evaluated in a number of different laboratories and with additional samples. This will help identify the applicability range and the limitations of the method and will define the interlaboratory method performance.

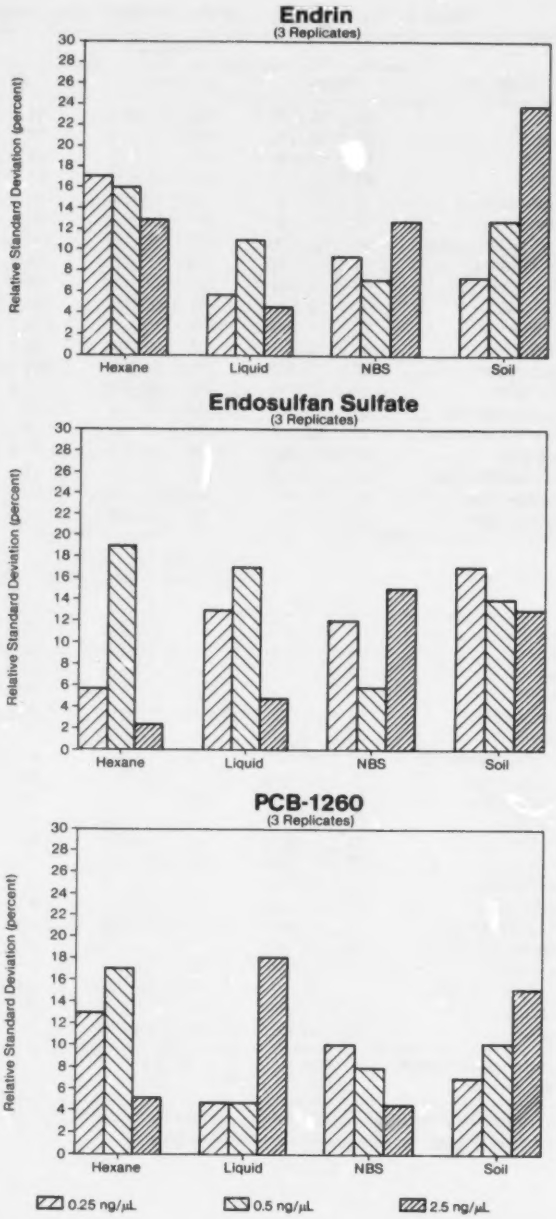

Figure 6. Distribution of relative standard deviations of average recoveries for endrin (top), endosulfan sulfate (middle), and Aroclor 1260 (bottom) for revised Method 8080.

When the revised Method 8080 is applied to samples that have not been previously characterized, confirmation of compounds identified in the sample may be required. Although the revised Method 8080 specifies a second capillary column for confirmation, additional work should be performed to determine the reliability of the identification obtained by the multicolumn technique. Determination of the OCPs and PCBs by gas chromatography/mass spectrometry (GC/MS) is an alternative that does not require fractionation of the extract by silica gel chromatography (3). With the GC/MS method, however, PCBs are identified and measured by level of chlorination. Furthermore, detection limits comparable to those obtained by using electron-capture detector may be difficult to achieve.

Table 7. Recoveries (%) of Method 8080 compounds from various spiked extracts of environmental samples

Compound	Hexane[a]			Liquid waste extract[a]		
	Concn 1	Concn 2	Concn 3	Concn 1	Concn 2	Concn 3
α-BHC	83 ± 16 (19)	106 ± 6.8 (6.4)	91 ± 4.6 (5.1)	96 ± 7.0 (7.3)	97 ± 3.5 (3.6)	79 ± 10 (13)
β-BHC	86 ± 15 (17)	110 ± 10 (9.5)	98 ± 2.0 (2.1)	92 ± 10 (11)	100 ± 4.0 (4.0)	90 ± 3.1 (3.4)
γ-BHC	85 ± 15 (18)	108 ± 11 (10)	99 ± 2.3 (2.3)	91 ± 10 (11)	100 ± 5.5 (5.5)	90 ± 4.0 (4.4)
δ-BHC	87 ± 12 (14)	109 ± 12 (11)	97 ± 1.6 (1.6)	[b]	[b]	90 ± 11 (8.8)
Heptachlor	79 ± 11 (13)	94 ± 9.5 (10)	83 ± 6.6 (7.9)	89 ± 14 (15)	94 ± 10 (11)	90 ± 11 (12)
Aldrin	88 ± 11 (13)	107 ± 9.5 (8.9)	89 ± 4.2 (4.7)	96 ± 8.9 (9.3)	98 ± 9.4 (9.6)	92 ± 9.2 (10)
Heptachlor epoxide	94 ± 6.7 (7.1)	109 ± 14 (13)	100 ± 23 (23)	111 ± 17 (15)	109 ± 14 (13)	89 ± 4.1 (4.6)
γ-Chlordane	94 ± 13 (14)	110 ± 11 (10)	91 ± 1.2 (1.3)	100 ± 8.5 (8.5)	103 ± 2.5 (2.4)	95 ± 8.0 (8.4)
Endosulfan I	89 ± 12 (14)	108 ± 13 (12)	99 ± 2.3 (23)	95 ± 6.5 (6.8)	100 ± 12 (12)	88 ± 3.8 (4.3)
4,4′-DDE	92 ± 13 (14)	107 ± 15 (14)	89 ± 4.5 (5.0)	119 ± 11 (8.9)	113 ± 2.5 (2.2)	95 ± 16 (17)
Dieldrin	89 ± 12 (14)	112 ± 13 (12)	102 ± 1.5 (1.5)	88 ± 3.2 (3.6)	86 ± 9.2 (11)	82 ± 4.3 (5.3)
Endrin	66 ± 11 (17)	65 ± 10 (16)	64 ± 8.3 (13)	101 ± 5.9 (5.8)	90 ± 10 (11)	65 ± 3.1 (4.7)
Endosulfan II	86 ± 7.9 (9.2)	111 ± 14 (13)	101 ± 0.6 (0.6)	[b]	[b]	79 ± 7.1 (9.0)
4,4′-DDD	89 ± 12 (14)	110 ± 9.8 (8.9)	97 ± 1.7 (1.8)	[b]	[b]	76 ± 16 (21)
Endrin aldehyde	83 ± 8.3 (10)	102 ± 19 (19)	95 ± 3.0 (3.2)	[b]	[b]	[b]
Endosulfan sulfate	91 ± 5.2 (5.7)	112 ± 21 (19)	104 ± 2.5 (2.4)	132 ± 17 (13)	127 ± 22 (17)	83 ± 4.0 (4.8)
4,4′-DDT	74 ± 19 (26)	88 ± 13 (15)	73 ± 5.8 (8.0)	101 ± 23 (23)	83 ± 11 (13)	88 ± 18 (21)
4,4′-Methoxychlor	98 ± 2.6 (2.7)	104 ± 18 (17)	104 ± 3.2 (3.1)	49 ± 14 (29)	58 ± 9.3 (16)	75 ± 4.6 (6.1)
Aroclor 1016	94 ± 14 (15)	93 ± 6.5 (7.0)	93 ± 2.0 (2.2)	114 ± 6.0 (5.3)	122 ± 10 (8.3)	118 ± 9.8 (8.3)
Aroclor 1260	92 ± 12 (13)	87 ± 15 (17)	78 ± 4.0 (5.1)	99 ± 4.6 (4.6)	102 ± 4.7 (4.6)	100 ± 18 (18)

	NBS SRM-1645 extract[a]			Sandy loam soil extract[a]		
	Concn 1	Concn 2	Concn 3	Concn 1	Concn 2	Concn 3
α-BHC	73 ± 2.1 (2.9)	75 ± 6.0 (8.0)	76 ± 5.6 (7.3)	86 ± 9.5 (11)	87 ± 4.9 (5.7)	89 ± 2.5 (2.8)
β-BHC	88 ± 4.1 (4.7)	94 ± 3.0 (3.2)	92 ± 7.1 (7.7)	94 ± 8.4 (8.9)	90 ± 4.1 (4.5)	93 ± 5.0 (5.4)
γ-BHC	83 ± 3.0 (3.6)	89 ± 4.1 (4.6)	93 ± 8.1 (8.7)	92 ± 11 (12)	91 ± 3.0 (3.3)	95 ± 4.6 (4.8)
δ-BHC	85 ± 4.6 (5.4)	92 ± 5.2 (5.6)	94 ± 8.7 (9.3)	94 ± 12 (13)	89 ± 3.6 (4.1)	93 ± 6.1 (6.5)
Heptachlor	53 ± 10 (19)	70 ± 7.7 (11)	88 ± 4.1 (4.7)	89 ± 9.6 (11)	83 ± 8.7 (11)	79 ± 17 (21)
Aldrin	69 ± 3.6 (5.2)	65 ± 4.6 (7.1)	72 ± 1.0 (1.4)	99 ± 4.4 (4.4)	88 ± 2.0 (2.3)	92 ± 12 (15)
Heptachlor epoxide	91 ± 4.9 (5.4)	91 ± 5.7 (6.3)	93 ± 8.6 (9.2)	96 ± 11 (11)	90 ± 4.6 (5.1)	94 ± 6.6 (7.0)
γ-Chlordane	77 ± 5.3 (6.9)	81 ± 4.9 (6.1)	85 ± 1.0 (1.2)	100 ± 8.3 (8.3)	93 ± 3.0 (3.2)	87 ± 11 (13)
Endosulfan I	85 ± 5.5 (6.5)	88 ± 5.1 (5.8)	91 ± 9.1 (10)	95 ± 10 (11)	89 ± 5.3 (5.9)	93 ± 7.5 (8.1)
4,4′-DDE	75 ± 5.3 (7.1)	76 ± 7.1 (9.3)	84 ± 1.0 (1.2)	105 ± 14 (13)	93 ± 5.6 (6.0)	82 ± 11 (13)
Dieldrin	92 ± 8.6 (9.4)	85 ± 9.4 (11)	94 ± 10 (11)	113 ± 12 (11)	99 ± 4.6 (4.6)	93 ± 8.2 (8.8)
Endrin	100 ± 9.5 (9.5)	87 ± 6.4 (7.3)	76 ± 9.9 (13)	74 ± 5.6 (7.5)	60 ± 7.6 (13)	47 ± 11 (24)
Endosulfan II	80 ± 7.4 (9.2)	81 ± 4.5 (5.5)	91 ± 12 (13)	97 ± 14 (14)	86 ± 6.7 (7.8)	89 ± 11 (12)
4,4′-DDD	106 ± 6.4 (6.0)	85 ± 3.1 (3.6)	90 ± 7.2 (8.0)	103 ± 9.6 (9.3)	88 ± 7.8 (8.9)	90 ± 7.8 (8.6)
Endrin aldehyde	70 ± 5.7 (8.2)	71 ± 9.2 (13)	88 ± 12 (14)	86 ± 11 (13)	82 ± 7.6 (9.3)	73 ± 20 (28)
Endosulfan sulfate	75 ± 8.7 (12)	86 ± 5.0 (5.8)	72 ± 11 (15)	112 ± 19 (17)	91 ± 13 (14)	88 ± 11 (13)
4,4′-DDT	54 ± 13 (24)	61 ± 7.9 (13)	76 ± 2.5 (3.3)	107 ± 25 (23)	83 ± 5.3 (6.5)	64 ± 14 (21)
4,4′-Methoxychlor	[b]	99 ± 17 (17)	92 ± 17 (19)	91 ± 14 (15)	89 ± 9.6 (11)	86 ± 14 (16)
Aroclor 1016	104 ± 9.0 (8.7)	104 ± 2.5 (2.4)	102 ± 4.6 (4.5)	90 ± 15 (17)	92 ± 4.5 (4.9)	85 ± 10 (12)
Aroclor 1260	92 ± 9.5 (10)	95 ± 7.5 (7.9)	91 ± 4.0 (4.4)	99 ± 6.8 (6.9)	89 ± 8.9 (10)	85 ± 13 (15)
Concn, ng/μL extract	0.25	0.5	2.5	0.25	0.5	2.5
No. of detns	3	3	3	3	3	3

[a] Triplicate determinations; value in parentheses is relative standard deviation.
[b] Unable to determine recovery because of interferences.

NOTICE

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